

FISCHER-TROPSCH SYNTHESIS FOR CLEAN TRANSPORTATION FUELS

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INTRODUCTION

The Fischer-Tropsch Synthesis (FTS) is a well established process for the production of synfuels (e.g., 1,2). Today, the process is practiced commercially in South Africa by Sasol and Mossesburg and in Malaysia by Shell and partners (3). While FTS was initially envisioned as a means of producing transportation fuels, operators, such as Sasol, have recognized that the recovery of chemicals and/or chemicals feedstock provides a means of improving the profits derived from the commercial operations (e.g., 4). However, while chemicals production may be a very profitable business option for the initial FTS plant operators, as more plants are brought on-stream this will become less profitable as surpluses will drive down the prices of chemical feedstocks. Thus, the ultimate basis for FTS must be the production of transportation fuels.

The FTS process has a decided disadvantage in that the product distribution follows a normal polymerization distribution for a C_n monomer. Thus, the plot of the log of the moles of each carbon number product versus the carbon number produces a straight line which is defined by alpha, which depends upon the rate of the propagation and termination steps. Furthermore, the value of alpha uniquely determines the product distribution such that illustrated in figure 1 (3). Today, most view the commercialization of FTS as requiring one of two options: (1) the production of heavy wax products which are subsequently hydrocracked to produce transportation fuel range products (e.g., the Shell middle distillate process (SDS); (5) and (2) the conversion of heavy products using a ZSM-5 type of catalyst (e.g., 6).

Because of the highly exothermic nature of the FTS, the ability to utilize a slurry reactor is very desirable (7). However, this operation requires the separation of the catalyst/wax slurry. When operating in a high wax mode in the temperature range of 230°C, more than half of the product must be processed to effect catalyst separation. Iron catalysts are attractive because of the highly olefinic nature of the products and because of the activity for the water-gas-shift (WGS) reaction that permits use of low H₂/CO ratios obtained by gasification of coal. However, unsupported iron catalysts have poor attrition resistance and supported catalysts have not been developed that have sufficient activity for commercial operation. Thus, one of the major operational problems associated with the use of an iron catalyst for FTS in a slurry reactor is catalyst/wax separation.

EXPERIMENTAL

The catalyst was prepared by continuous precipitation from an aqueous solution of iron nitrate containing silica derived from the hydrolysis of tetraethyl silicate using ammonia. Potassium was added to the washed and dried catalyst to provide a composition containing (atomic ratio) 100Fe/4.4Si/1.0K (8). The catalyst was activated in a flow of CO at 270°C and 175 psig during 24 hours. Following activation, synthesis was effected using a H₂/CO = 0.7 feed, 270°C, 175 psig and 3.4 NL/hr.g(Fe). Products were analyzed using a Carle gas analyzer for the gaseous products and g.c. with a DB-5 column for the liquid hydrocarbon products (9).

RESULTS AND DISCUSSION

A high activity iron catalyst has been prepared by precipitation; furthermore, this catalyst has a stable activity such that the decline in CO conversion is less than 1%/week during six months of operation. This catalyst produces a "low alpha" product distribution (figure 2). While this particular run was terminated after 2,000 hours (figure 3), this catalyst has been utilized for runs lasting longer than 4,000 hours with a similar slow decline in activity. When operating in this mode with an alpha value of 0.72 and assuming ideal gas and solution behavior, essentially all of the products would exit the reactor in the vapor phase (10). Thus, while a small contribution of a two-alpha product distribution (e.g., 11) and deviation from nonideality of the gas and/or liquid products may be operable, essentially all of the products should exit the reactor in the gas phase. **Provided this does occur, catalyst-wax separation would not be required.** Even if a small fraction of the product does not exit the reactor in the vapor phase, the ability to activate the catalyst external to the slurry reactor would permit catalyst to be added to make up for the small daily loss of catalyst in any liquid phase products that must be removed from the reactor. This

would permit the catalyst to be utilized in the form of 1-3 micron particle sizes that result from the precipitation and activation procedure rather than having to form the precipitated catalyst into particles in the 50-100 micron range as apparently has been practiced at Sasol (11).

The kinetics of the FTS is such that the productivity of hydrocarbons depends dramatically upon the conversion of CO (12). Thus, at low CO conversion the rate of production of hydrocarbons is much higher than it is at higher CO conversion levels. At the same time, the rate of the WGS reaction is low at low CO conversions but increases as the conversion of CO increases so that at about 50-60% CO conversion the rates of hydrocarbon production and the WGS reaction become about equal and remain so as the CO conversion increases further. This is illustrated in figure 4 showing that the H_2/CO ratio initially decreases with increasing CO conversion, attains a minimum and then increases to the value of the feed gas (defined here as the equivalence point); at CO conversions above the equivalence point the reaction produces hydrogen as well as hydrocarbons and CO_2 . In order to take advantage of the higher rate and higher selectivity for hydrocarbons, it has been proposed that the FTS reactor be operated at CO conversion levels that are at or below the equivalence point (12).

The hydrocarbon product distribution obtained at a CO conversion level above the equivalence point is shown in Table 1. If the reactor is operated at the equivalence point or even lower CO conversions, the alkene concentrations will be higher than shown in Table 1. Thus, the following should be viewed as the minimum hydrocarbon productivity levels that could be obtained by incorporation of the process consideration described below. The Conversion of Olefins to Diesel and Gasoline (COD) process has been developed by CEF of South Africa and Lurgi of Germany and a proprietary catalyst for this process has been developed by Süd-Chemie and CEF (13). The catalyst has been utilized at the Moss gas plant in South Africa with a through-put of 68 tons/hour. The Moss gas facility is able to utilize a stream that contains oxygenates (1.5-20 wt.%) saturated with water. In this manner, the C_{2-4} olefins shown in table 1 could be converted to transportation fuel. Thus, the gasoline range (C_{4-10}) yield would be about 47% of the product from the low-alpha operation. In addition, the C_{11+} fraction could be hydrotreated as is done in the SDS process to produce even more gasoline as well as high quality diesel.

In summary, the above considerations would provide a means to eliminate the need to effect catalyst-wax separation that would allow catalyst to either be retained within or recycled to the reactor. Whether this proposed option would be a viable one would depend upon the economic impact of the higher amount of methane and ethane that are produced as well as the cost differential between the COD oligomerization and the hydrocracking processes. It appears that the potential advantages would merit an economic evaluation.

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Table 1 Products from the Conversion of Syngas Using a Low- α Iron Catalyst		
Carbon Number	Product, wt. %	Olefin, wt. %
1	7.88	---
2	6.45	1.29
3	10.5	7.22
4	8.23	5.72
5	7.46	4.88
6	6.22	3.98
7	5.85	3.58
8	4.50	2.58
9	3.41	1.83
10	3.01	1.53
11+	36.5	---

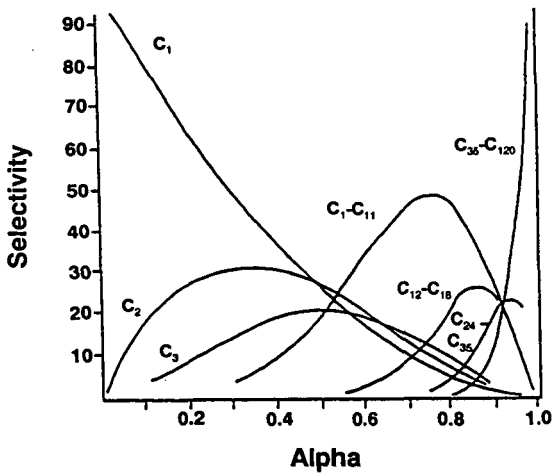


Figure 1. Product distribution dependence upon α .

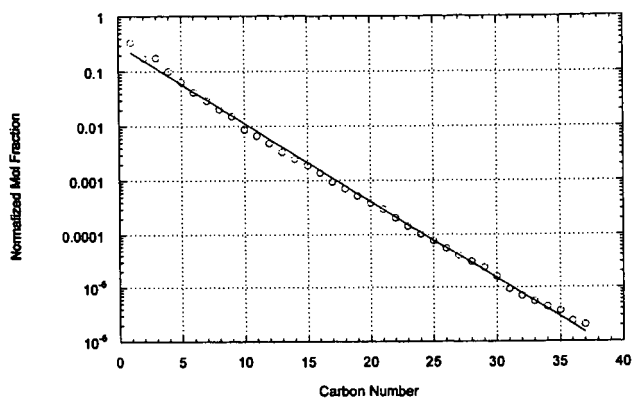


Figure 2. Anderson-Schulz-Flory plot of the products obtained from synthesis with a low- α (0.72) iron catalyst.

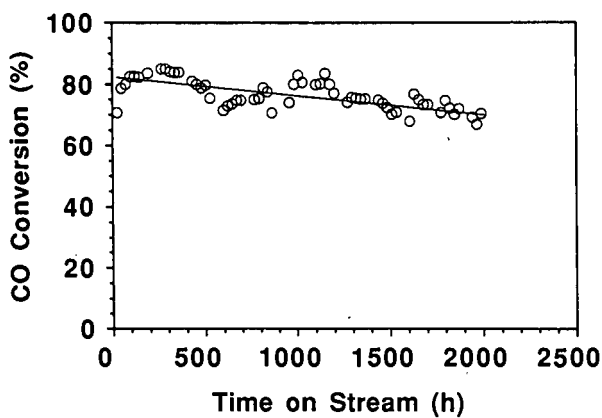


Figure 3. CO conversion with a low- α iron catalyst with time-on-stream.

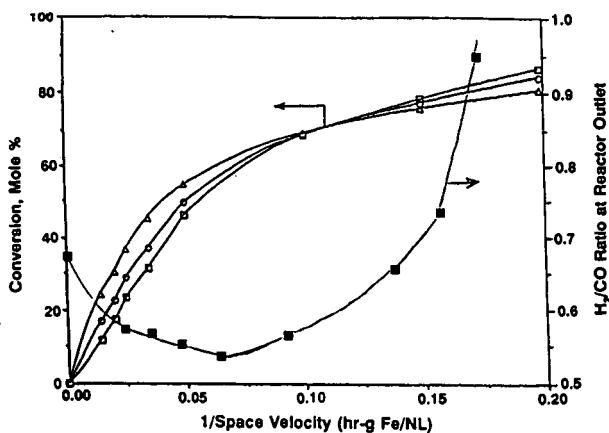


Figure 4. The conversion of CO (\square), H_2 (Δ), ($\text{CO} = \text{H}_2$) (\circ) and the H_2/CO ratio at the reactor exit (\blacksquare) for a low- α iron catalyst.